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On the Compounds of Urea and Benzoic Acid

By

Yukichi Osaka and Kinji Ando

(Received May 31, 1921)

Dessaignes obtained a compound of urea and benzoic acid of the composition, $2CO(NH_2)_2 . C_6H_5.CO_2H$, from their solution in absolute alcohol as leafy crystals.[1] Suggested by this, the equilibrium of the system of urea, benzoic acid and ethyl alcohol was studied to see whether there was no other compound could be obtained from them.

Ethyl alcohol was purified by distilling commercial absolute alcohol over calcium oxide. It was 99·50 per cent. by weight pure. Benzoic acid was purified by recrystallisation from water and urea by recrystallisation from alcohol.

The materials were put in an Erlenmeyer flask of ca. 20 cc. capacity, well stoppered with a cork and covered with a sheet of oil-paper. It was made to rotate in a thermostat at 25° for at least two days and nights. When equilibrium was attained, the solution and the residue[2] were analysed separately. Benzoic acid was determined by titration with N/10-baryta water, and urea by Kjeldahl's method, the ammonia formed being absorbed in a given amount of N/5-hydrochloric acid and then titrated back with N/10-baryta water. In the calculation the alcohol was assumed to be anhydrous.

The results are given in Tables 1 and 2. In Table 1 the com-

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1 Beilstein, II, p. 1136, from Jahrb. Fortschr. d. Chem., 1857, 545.

2 The residue was not completely freed from the mother liquor.

positions of the solutions and the residues are denoted in gram percentages and in Table 2 they are represented by the formula :

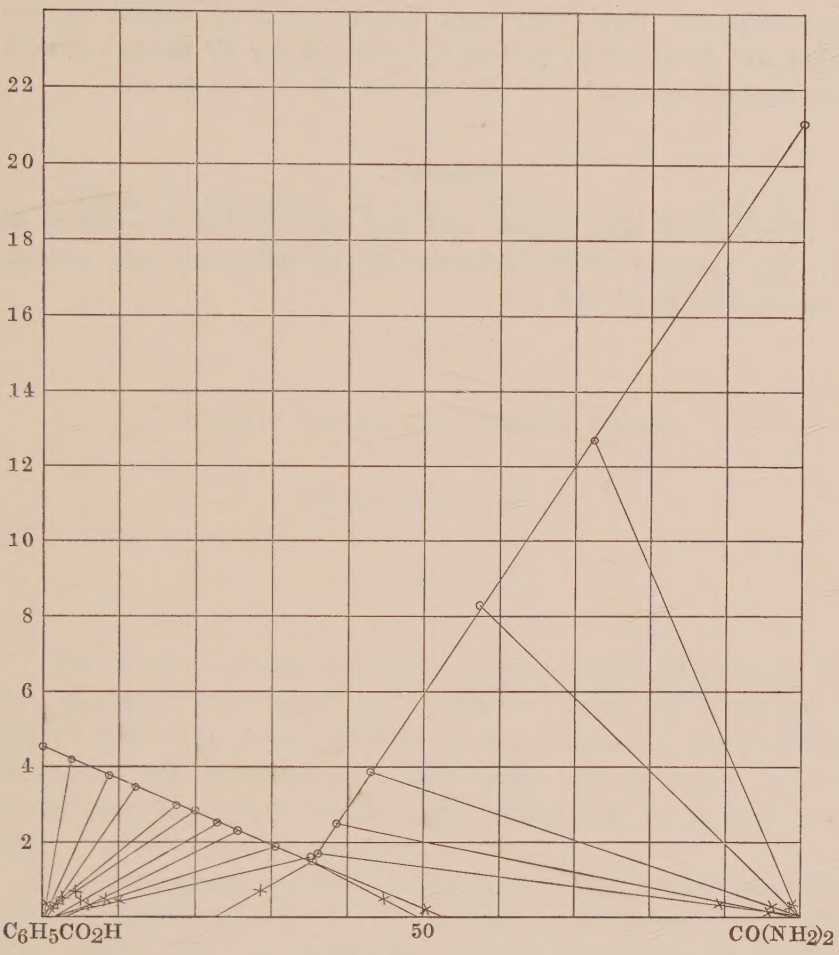
$$100\,m\,C_2H_5OH,\ x\,C_6H_5CO_2H,\ y\,CO(NH_2)_2.$$

Table 1.

No.	Solution.			Residue.		
	$C_6H_5CO_2H$	$CO(NH_2)_2$	C_2H_5OH	$C_6H_5CO_2H$	$CO(NH_2)_2$	C_2H_5OH
1	36·92	—	63·08	—	—	—
2	37·64	0·72	61·64	86·56	0·33	13·11
3	38·55	1·81	59·64	86·99	0·47	12·54
4	39·38	2·64	57·98	86·93	0·86	12·21
5	40·75	4·22	55·03	83·99	1·12	14·89
6	41·56	5·10	53·34	77·44	1·78	20·78
7	42·31	6·11	51·58	81·77	2·21	16·02
8	42·90	7·09	50·01	85·73	2·71	11·56
9	44·68	9·67	45·65	81·30	3·59	15·11
10	45·55	12·12	42·33	80·73	4·43	14·84
11	46·24	12·48	41·28	62·35	12·27	25·38
12	46·23	12·50	41·27	57·01	23·34	19·65
13	46·20	12·56	41·24	62·17	31·24	6·59
14	43·78	12·15	44·07	15·67	67·76	16·57
15	35·06	12·76	54·18	7·19	81·51	11·30
16	25·38	9·41	65·21	5·94	79·07	14·99
17	11·22	7·39	81·39	2·30	79·54	18·16
18	5·06	6·59	88·35	1·38	79·58	19·04
19	—	5·82	94·18	—	—	—

Table 2.

No.	Solution.			Residue.		
	$C_6H_5CO_2H$	$CO(NH_2)_2$	C_2H_5OH	$C_6H_5CO_2H$	$CO(NH_2)_2$	C_2H_5OH
1	100·00	0	4·53	—	—	—
2	96·26	3·74	4·18	99·23	0·77	0·40
3	91·29	8·71	3·75	98·91	1·09	0·38
4	88·03	11·97	3·43	98·03	1·97	0·36
5	82·61	17·39	2·96	97·36	2·64	0·45
6	80·03	19·97	2·85	95·53	4·47	0·68
7	77·30	22·70	2·50	94·79	5·21	0·49
8	74·42	25·58	2·30	93·96	6·04	0·34
9	69·45	30·55	1·88	91·76	8·24	0·45
10	64·90	35·10	1·60	89·96	10·04	0·44
11	64·57	35·43	1·53	71·43	28·57	0·77
12	64·53	35·47	1·53	55·14	44·86	0·49
13	64·41	35·59	1·52	49·47	50·53	0·14
14	63·93	36·07	1·70	10·22	89·78	0·29
15	61·58	38·42	2·52	4·16	95·84	0·17
16	57·02	42·98	3·88	3·56	96·44	0·24
17	42·76	57·24	8·22	1·40	98·60	0·29
18	27·43	72·57	12·68	0·85	99·15	0·31
19	0	100·00	21·11	—	—	—



With the data in Table 2, Fig. 1 was obtained. As may be seen, there is no evidence of the existence of any compound between benzoic acid and urea. The presence of 0·5 per cent. of water might be the cause of the non-formation of the compound, but whether Dessaignes worked with perfectly dry alcohol or not is unknown, as the original paper was not accessible to us.

A few solubility determinations were carried out at other temperatures, 0° and 40°, but the result was practically the same.

Then some qualitative experiments were tried under different conditions. The two solid components were once completely dissolved in alcohol by warming and allowed to crystallise on cooling. This was repeated in a sealed tube with alcohol dried over anhydrous

copper sulphate. Again they were dissolved in much alcohol and the solvent was driven off by passing a current of dry air through it until some crystals separated out. But all our efforts were in vain.

Summary.

A system of urea, benzoic acid and ethyl alcohol was studied at 25°. No evidence of the existence of any compound was noticed. It was so also at 0° and 40°.

The Tungsten X-Ray Spectrum with a Mica Spectrometer

By

Usaburo Yoshida and Shinsuke Tanaka

(Received June 14, 1921)

The X-ray spectrum belonging to the L-series of tungsten has been throughly investigated by Dershem,[1] Overn[2] and Siegbahn[3] in recent years. The results obtained by these authors on the prominent lines are in fair agreement with each other. But in regard to some of the faint lines there remain some ambiguities as to their wave lengths and even to their existence.

The arrangement employed in the present experiment is essentially the same as that used in the former experiment[4] carried out by one of the writers. The X-rays from the tungsten anticathode of a Coolidge tube is analysed by a bent mica spectrometer which is represented diagramatically in Fig. 1. Here B is a lead box, S the slit the width of which is 0.15 mm., C is a wooden cylinder of radius 36.10 mm. and on its surface a sheet of mica of a thickness of 0.06 mm. is just fastened. Consequently the value of 36.16 mm. is taken as the radius of ths cylindrical mica. The perpendicular distance SA from the slit S to the film side of the photographic plate P is represented by a, the perpendicular distance from the center of the cylindrical mica to

1 Dershem, Phys. R., **11**, 471, (1918).
2 Overn, Phys. R., **14**, 137, (1919).
3 Siegbahn, Phil. Mag., **38**, 639, (1919).
4 Yoshida, Mem. Coll. Sci., Kyoto, **4**, 343, (1921).

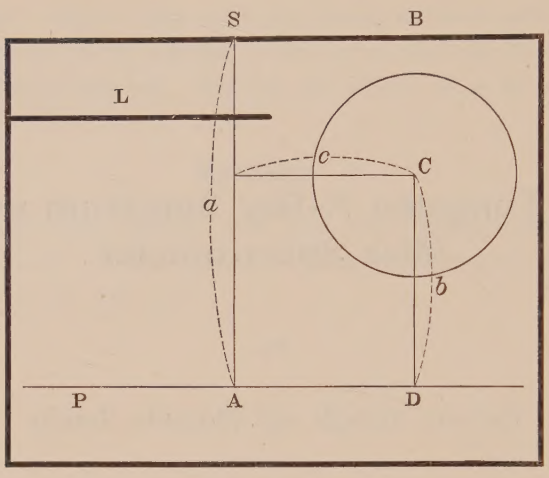


Fig. 1.

the film side of the photographic plate and that to the line SA are represented by b and c respectively. The values of a, b and c are not the same throughout the experiment and their numerical values corresponding to the three photographic plates measured in the present experiment are given in Table I.

TABLE I.

	a in mm.	b in mm.	c in mm.
Plate No. 3 ...	235.8	137.9	57.1
Plate No. 4 ...	196.8	97.2	57.1
Plate No. 5 ...	157.4	60.1	56.6

The photographic plates No. 3 and No. 5 are reproduced in the annexed figure. In the case of the plate No. 3, the distance b was very large, and consequently the greatest dispersion was attained in this case. On the contrary, in the case of the plate No. 5, the photographic plate was brought nearest to the cylindrical mica ; and the spectral lines of longer wave lengths were obtained in this case by sacrifice in the dispersion. Here it is to be noted that many faint lines which were visible on the original plate are absent in the reproduction.

The time of exposure was from 30 to 50 hours, using the current of the order of from 4 to 7 milliamperes and the potential differences

of the order of several ten kilovolts. All of the prominent lines of the L-series of tungsten were visible in all the orders up to the fifth or more. Moreover many weak lines showed themselves in the photographs. The wave lengths of these weak lines which were in the region of shorter wave lengths than the fifth order spectrum of the L-series were determined by interpolation from the wave lengths of the lines α_2 α_1 β_4 β_1 β_3 β_2 γ_1 of the L-series given by Siegbahn.[1] The grating constant of the mica now used was calculated from the wave lengths of the prominent lines of the L-series of tungsten, the values of a, b, c and the radius of the cylindrical mica mentioned before. The value of this grating constant thus calculated came out to be 9,858 Å.U. The wave lengths of the many weak lines which were in the region of longer wave lengths than the fifth order spectrum of the L-series were calculated from the values of this grating constant, a, b, c and the radius of the cylindrical mica mentioned before.

Most of the weak lines in the region of the shorter wave lengths than the fifth order spectrum of the L-series appeared both in the third and the fifth order, and some in the fourth as shown in Table II. The wave lengths of these lines determined from the photographs No. 3, No. 4 and No. 5, and also their average values are given in

TABLE II.

Wave lengths in Å.U.

lines	Plate No. 3				Plate No. 4			Plate No. 5			
	third order	fourth order	fifth order	means	third order	fifth order	means	third order	fourth order	fifth order	means
η	—	1.414	—	1.414	—	—	—	—	1.414	1.415	1.414^5
	1.287	1.288	1.287^4	1.287^5	1.289	1.287^8	1.288^4	1.287	1.288	1.286	1.287^0
	1.236^5	—	1.237^3	1.236^9	1.234	1.236	1.235^0	—	—	1.235^4	1.235^4
	1.221	—	1.221^4	1.221^4	—	1.222	1.222	—	—	1.220^6	1.220^6
	1.211	—	1.212	1.211^5	1.210	1.211	1.210^5	—	—	1.212^8	1.212^8
β_5	1.202	—	1.200	1.201^0	1.202	1.201	1.201^5	—	—	1.200^6	1.206^6
	1.130	—	1.129	1.129^5	1.128	—	1.128	—	—	—	—
	1.070	—	1.071^4	1.070^7	1.072	1.071	1.071^5	—	—	—	—
γ_2	1.065	1.064	1.065^4	1.064^8	1.065	1.064	1.064^5	1.065	—	—	1.065
γ_3	1.059	1.058^5	1.059	1.058^8	1.058	1.060	1.059^0	1.057^7	—	—	1.057^7
γ_4	1.025	—	1.025^4	1.025^2	1.025	—	1.025	1.025	—	—	1.025

1 Siegbahn, loc. cit.

TABLE III.

Wave lengths in Å.U.

lines	Siegbahn	Dershem	Overn	Plate No. 3	Plate No. 4	Plate No. 5	mean value
l	1.67505	—	—	—	—	—	—
α_2	1.48452	1.482^{8}	1.483^{9}				
α_1	1.47348	1.472^{2}	1.473^{1}				
η	1.4177	1.416^{3}	—	1.414	—	1.414^{5}	1.414^{3}
β_4	1.29874	1.297^{7}	1.298^{4}				
	1.2871	1.286^{3}	1.287^{2}	1.287^{5}	1.288^{4}	1.287^{0}	1.287^{6}
β_1	1.27917	1.278^{4}	1.279^{3}				
β_3	1.26000	1.258^{6}	1.259^{8}				
β_2	1.24191	1.241^{6}	1.243^{4}				
	1.2395	—	1.235^{5}	1.236^{9}	1.235	1.235^{4}	1.235^{8}
	1.2205	1.220^{2}	1.221^{2}	1.221^{2}	1.222	1.220^{6}	1.221^{3}
	1.2118	—	1.213^{2}	1.211^{5}	1.210^{5}	1.212^{8}	1.211^{6}
	—	1.209^{8}	1.209^{7}	—	—	—	—
β_5	1.2031	—	1.202^{1}	1.201	1.201^{5}	1.200^{6}	1.201^{0}
	—	1.177^{3}	—	—	—	—	—
	1.1284	1.129^{2}	1.130^{2}	1.129^{5}	1.128	—	1.128^{8}
γ_1	1.09553	1.095^{3}	1.096^{7}				
	—	—	1.079^{4}	—	—	—	—
	—	1.070^{5}	1.072^{4}	1.070^{7}	1.071^{5}	—	1.071^{1}
γ_2	1.06584	1.064^{8}	1.065^{9}	1.064^{8}	1.064^{5}	1.065	1.064^{8}
γ_3	1.05965	1.058^{7}	1.059^{6}	1.058^{8}	1.059	1.057^{7}	1.058^{5}
	—	1.042^{7}	1.044^{6}	—	—	—	—
γ_4	1.02647	1.025^{3}	1.026^{3}	1.025^{2}	1.025	1.025	1.025^{1}
	—	—	$.792^{8}$	—	—	—	—
	—	—	$.710^{8}$	—	—	—	—
	—	$.706^{8}$	$.706^{5}$	—	—	—	—
	—	—	$.629^{1}$	—	—	—	—

Table II and Table III. The wave lengths of the spectrum lines belonging to the L-series obtained by Siegbahn, Dershem and Overn are, for the sake of reference, also given in Table III. The wave lengths of most of the lines, excepting a few, were in fair agreement with those given by the other authors. For the line η the wave length obtained in the present experiment came out somewhat smaller than those given by Siegbahn and Dershem. For the line 1.2395 Å.U. of Siegbahn the writers' value is smaller by 0.0037 Å.U., the value being 1.235^{8} Å.U., which is in fair agreement with that given by Overn. The line 1.071^{1} Å.U. observed in the present experiment seems to be the same as that obtained by Dershem and Overn at 1.070^{5} Å.U.

and 1.072[4] Å.U. respectively. As this line under consideration appeared both in the third and the fifth order spectrum of the plates No. 3 and No. 4, there seems to be no doubt as for its real existence. Lastly it must be noted that the values of the wave lengths of the prominent lines of the L-series were omitted in the Table II and III, for the Siegbahn's values for the wave lengths of these lines were relied on in determining the wave lengths of the other weak lines given in these tables.

It was already stated that many weak and diffuse lines made their appearance in the region of longer wave lengths than the fifth order spectrum of the L-series as is seen in the plate No. 5. The wave lengths of these lines were calculated, for the present, by considering that they were due to the so-called reflection from the cleavage surface of the cylindrical mica. Here it must be remarked that, as these lines were very diffuse, their wave lengths thus determined would not be accurate. Many of these lines were seen in the positions of the prominent lines of the L-series in the higher orders than the fifth as shown in Table IV. The wave lengths calculated are in accordance with those given by Siegbahn and others within the limit of experimental errors. From such consideration, it may be concluded that with a mica X-ray spectrometer the X-ray spectrum of the L-series of tungsten are obtainable up to the seventh and even up to the tenth order.

TABLE IV.

Wave lengths in Å.U.

6th order	7th order	8th order	9th order	10th order	Wave lengths given by Siegbahn	lines
1.098	1.099	1.098	1.105(?)	1.095	1.09553	γ_1
1.244	1.245	1.244	—	—	1.24191	β_2
—	1.262	—	—	—	1.26000	β_3
1.283	1.282	—	—	—	1.27917	β_1
1.299	1.291	—	—	—	1.29874	β_4
1.479	1.486	—	—	—	1.48452	α_1

TABLE V.

Wave lengths in Å.U.

7.90	9.28	10.25
8.06	9.42	10.62
8.16	9 59	10.77
8.59	10.04	

Besides the lines above stated, eleven lines of unknown origin were also detected in the photographs. Their wave lengths calculated in an ordinary way were tabulated in Table V. Of course it might be possible that these obscure lines were due to the reflections from the cylindrical mica in some unknown manner; and the values of the wave lengths given in Table V must be regarded as a mere indication of their positions on the photographic plate in reference to the other determinate lines of known origin.

In conclusion the writers wish to express their hearty thanks to Prof. Mizuno for the interest he has taken in the research.

Plate No. 3

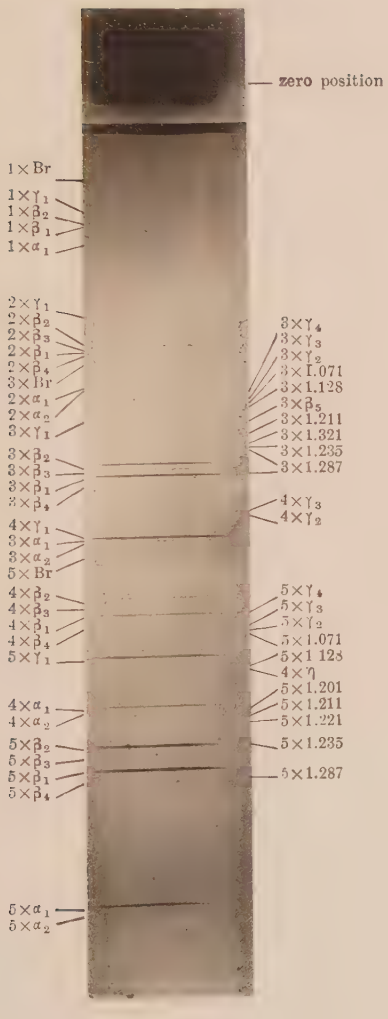
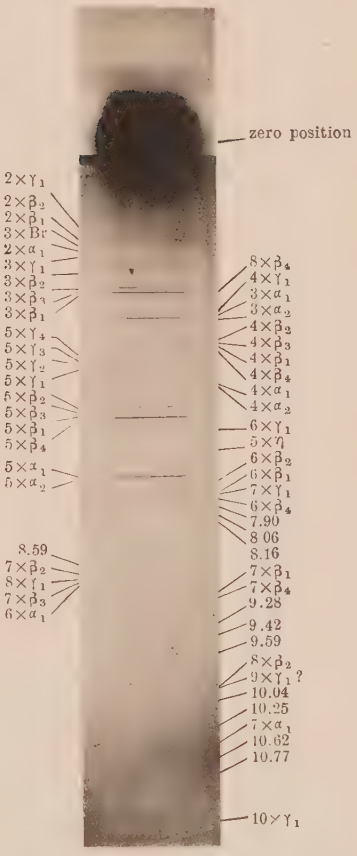


Plate No. 5



Condensation of Nitriles with Thiamides
I. Benzonitrile and Thiobenzamide

By

Seiichi Ishikawa

(Received June 20, 1921)

About 10 years ago M. Matsui[1] isolated a condensation-product from thiobenzamide and benzonitrile by passing dry hydrochloric acid gas into their ethereal solution cooled with a freezing mixture, and named it benzimino-sulphide based on the assumption that the condensation takes place according to the following equation:

$$C_6H_5-C(=NH)-SH \;+\; C_6H_5-C\equiv N \;=\; C_6H_5-C(=NH)-S-C(=NH)-C_6H_5$$

In the condensation-reactions of this kind, benzimino-chloride is generally considered to be produced as an intermediate product, which further reacts so as to form the final condensation-product. If, therefore, the condensation-product is really benziminosulphide as above assumed, it may be expected that the same substance will be produced by the interaction of benzimino-chloride and thiamide. So Matsui[2] made many trials to prepare the similar substances by using imono-chlorides; but he never could succeed, the only substances he could isolate were found similar to those obtained by S. Jamieson[3] under similar treatment. Thus suspicion naturally arose as to the constitution

1 Mem. Coll. Sci. Eng., Kyoto **2**, 401 (1910).

2 Hitherto not published.

3 Am. Chem. Soc. **26**, 179 (1904).

of the condensation-product, for which the benzimino isothio-benzamide formula is also assignable, assuming the condensation-reaction to proceed as follows:

$$C_6H_5-C=NH \quad + \quad C-C_6H_5 \quad = \quad C_6H_5-C=N-C-C_6H_5$$
$$\quad\quad | \quad\quad\quad\quad ||| \quad\quad\quad\quad\quad\quad | \quad\quad ||$$
$$\quad SH \quad\quad\quad\quad N \quad\quad\quad\quad\quad\quad SH \quad HN$$

The present investigation undertaken at the suggestion of Prof. M. Matsui with the object of making this ambiguous point clear, chiefly deals with the oxidation, reduction and alkylation of the condensation-product.

As Matsui[1] has already pointed out, the condensation-product is very oxidable and gives dibenzenylazosulphime as the oxidation-product. Now the formation of dibenzenylazosulphime from the condensation-product by oxidation can not be explained by the iminosulphide formula, unless we consider that the condensation-product is first decomposed into benzonitrile and thiobenzamide, and this latter undergoes oxidation thus:

$$2\,C_6H_5-C=NH \quad + \quad I_2 = C_6H_5-C\begin{matrix}=N\\ -S-N=\end{matrix}C-C_6H_5+H_2S+2HI \ldots\ldots(\mathrm{I})$$
$$\quad\quad | \quad\quad\quad\quad\quad\

but not such as is represented by the equation (I), that is, the theory that decomposition precedes oxidation, and thiamide, one of the decomposition-products undergoes oxidation so as to form dibenzenylazosulphime must be abandoned. Evidently this fact is sufficient to confirm the conclusion that the iminosulphide formula proposed beforehand is incorrect, and for that the benziminoisothiobenzamide formula must be adopted. Furthermore, the results of reduction and alkylation were both found in accord with that of oxidation to point out the correctness of the latter formula.

Reduction was conducted by warming the alcoholic hydrochloric acid solution with zinc on a water-bath till the evolution of hydrogen sulphide ceased, and as the chief reduction product benzylbenzamidine was obtained. Now the production of benzylbenzamidine and the evolution of hydrogen sulphide as the consequence of reduction may be conceived to occur, only when the condensation-product has the constitution represented by benziminoisothiobenzamide, in which the atomic linking $-C-N=C$ ($\|$ at N) combined with the SH group exists. In benziminosulphide as sulphur is linked to two carbon atoms, we can but expect benzylamine as the reduction-product, which may be formed with the elimination of sulphur.

Alkylation of the condensation-product with ethyl iodide readily takes place and gives rise to a product in which the ethyl radical is evidently combined with sulphur, as it is very unstable in the free state and instantly decomposes into ethyl mercaptane and cyaphenine exactly similar to the alkylation-product of thiobenzamide[1], thus affirming the presence of the SH group in the condensation-product.

From these results the author has come to the conclusion that the iminosulphide formula once given by Matsui to the condensation-product of benzonitrile and thiobenzamide must now be rejected, and for it the benziminoisothiobenzamide formula should be adopted.

Experimental Part

1. *Oxidation of the Condensation-product with Iodine*

The condensation-product of benzonitrile and thiobenzamide was

1 A. Bernthsen: Ann. d. Chem, **197**, 348 (1879).
M. Matsui: Mem. Coll. Sci. Eng. Kyoto, **2**, 40 (1909).

prepared according to Matsui's description,[1] that is by saturating dry hydrochloric acid gas in an ethereal solution of benzonitrile and thiobenzamide taken equimolecularly. The hydrochloride crystallized out after having been washed with ether, was decomposed by a soda solution, and the free condensation-product thus separated was extracted with ether and recrystallized from benzene. It is a very oxidable substance and easily changes into dibenzenylazosulphime as was described in Matsui's previous report. As this behaviour is vary analogous to that of thiobenzamide one may naturally doubt, whether it is not possible that the condensation-product is first decomposed into its components, and thiamide thus literated undergoes oxidation and yields dibenzenylazosulphime.

In order to decide this doubtful point clearly the oxidation reaction was studied quantitatively using iodine as the oxidizing agent as follows: 0.240 grams of the condensation-product dissolved in 20 c.c. of alcohol was added with 25 c.c. of $\frac{1}{10}$ normal iodine solution, and after shaking the mixture for a few minutes the excess of iodine was titrated with $\frac{1}{10}$ normal sodium thiosulphate. After the titration was over the solution was neutralized with sodium hydroxide, diluted with an excess of water, and the dibenzenylazosulphime which crystallized out was filtered, washed well, dried and weighed. The results obtained are shown below:

		Dibenzenylazosulphime		
$\frac{1}{10}$ N-Iodine (c.c.)	$\frac{1}{10}$ N-$Na_2S_2O_3$ (c.c.)	Calc. from Iodine	Calc. from original Substance	Found
25	5.6	0.231	0.238	0.234

The calculated value of dibenzenylazosulphime in the above table, obtained on the assumption that the oxidation takes place according to the equation given below agrees fairly well with the value actually found experimentally,

$$C_6H_5-C(=NH)-C(-HS)=C-C_6H_5 + I_2 = C_6H_5-C(=N-)-C(-S-)=C-C_6H_5 + 2HI$$

This decidedly confirms the view that the substance which undergoes oxidation is the condensation-product itself and not the thiamide, one of its decomposition-products. Moreover, if the formation of diben-

[1] loc. cit.

zenylazosulphime comes from the oxidation of thiobenzamide, its formation must always be accompanied by the evolution of hydrogen sulphide as is seen in the equation:

$$C_6H_5-C(=NH)-SH + HN=C(-HS)-C_6H_5 + I_2 = C_6H_5-C(=N-)-N=C(-S-)-C_6H_5 + 2HI + H_2S$$

In our experiment, however, no trace of hydrogen sulphide could be detected.

2. *Reduction of the Condensation-product*

In a flask containing an alcoholic solution of the condensation-product and zinc powder, a concentrated hydrochloric acid was added and the flask well shaken, whereupon reduction took place, and hydrogen sulphide was evolved. When the evolution of hydrogen sulphide stopped, hydrochloric acid was again added and the mixture shaken, and this process was repeated several times till the evolution of hydrogen sulphide became nearly imperceptible. The contents of the flask were now heated on a water bath under a reflux condenser to make the reduction complete. The solution after having been separated from zinc powder by filtration was treated with a concentrated sodium hydroxide solution to dissolve zinc hydroxide completely, when a yellowish oil separated out. The oily substance was extracted with ether, and into this ethereal solution an ethereal hydrochloric acid solution was added, and the mixture was evaporated to drive off the ether. By this treatment a small quantity of a yellow viscous substance first separated out and a larger quantity (about 1.5 grams from 4 grams of the condensation-product) of a white crystalline substance crystallized out on further evaporation. This white reduction product was recrystallized from water and was found to melt at 211–215°. Its platinum double salt obtained as yellow prismatic crystals melting at 148° was used for analysis, the result having been found to be as follows:

0.1250 gram of the double salt gave 0.0295 gram platinum on ignition

	Found	Calc. $(C_{14}H_{15}N_2Cl)_2$ Pt Cl_4
Pt	23.60	23.50%

From the result of this analysis there is no doubt that the white crystalline substance above obtained as the reduction-product is

benzylbenzamidine hydrochloride. The yellow viscous substance produced as the bye-product was not further examined.

3. *Alkylation of the Condensation-product*

About 3 grams of the condensation-product were mixed with 4 grams of ethyl iodide and the mixture was heated on a water bath for a few minutes. Reaction similar to the alkylation of thiobenzamide readily took place and gave the product which solidifies on cooling. The product was well washed with ether to remove the original substance and ethyl iodide left unchanged and was obtained as yellow monoclinic crystals. It is insoluble in ether, and when heated it darkens in colour at about 170°, melts at 181° and decomposes on a further heating, evolving iodine. The result of analysis was found to be as follows:

0.2049 gram of the substance gave 0.1211 gram silver iodide.

	Found	Calc. ($C_{16}H_{17}N_2SI$)
I	32.01	32.03%

Free S-ethyl benziminoisothiobenzamide was isolated as an oily substance by treating the hydroiodide with caustic soda. It is a very unstable substance and spontaneously decomposes into mercaptane and cyaphenine as ethyl thiobenzamide does.

The author desires to express his sincere thanks to Prof. M. Matsui for the interest he has taken throughout the work.

Sur les courbures des courbes gauches dans un espace non-euclidien de plusieurs dimensions

par

Teikichi Nishiuchi

(Reçu, le 21 juin 1921)

Soient $\xi_0, \xi_1, \ldots\ldots, \xi_n$ les coordonnées de Weierstrass d'un point dans un espace non-euclidien de n dimensions dont la courbure d'espace est $\frac{1}{k^2}$. Pour les coordonnées du point, nous pouvons prendre les nombres

$$x_0 = k\,\xi_0, x_1 = \xi_1, \ldots\ldots\ldots\ldots\ldots, x_n = \xi_n.$$

Soient

$$x_0 = \psi_0(t), x_1 = \psi_1(t), \ldots\ldots\ldots\ldots, x_n = \psi_n(t),$$

les formules qui donnent les coordonnées d'un point d'une courbe gauche Γ en fonction d'un paramètre t. Nous désignerons par $x'_i, x''_i, \ldots\ldots, x_i^{(r)}$ les dérivées première, seconde, ..., $r^{ième}$ de x_i par rapport à la variable t, et nous supposerons ici que $x_0, x_1, x_2, \ldots\ldots, x_n$ admettent des dérivées jusqu'à l'ordre n.

Prenons les $r+1$ points $P_0[x(t)]$, $P_1[x(t+\triangle t)]$, ... $P_r[x(t+r\triangle t)]$ de la courbe Γ. Alors on trouve que les coordonnées du pôle absolu ${}_rQ$ du r point[1] $(P_0, P_1, \ldots\ldots, P_{r-1})$ dans le $r+1$ point $(P_0, P_1, \ldots\ldots, P_{r-1}, P_r)$ sont

---

1 Voir le memoir de D'Ovidio. Math. Ann., t.12, p. 403.

$$ {}_ry_i = \frac{\begin{vmatrix} (xx) & (xx') & \cdots & (xx^{r-1}) & x_i \\ (x'x) & (x'x') & \cdots & (x'x^{r-1}) & x'_i \\ \vdots & \vdots & & \vdots & \vdots \\ (x^r x) & (x^r x') & \cdots & (x^r x^{r-1}) & x^r_i \end{vmatrix}}{\sqrt{\begin{vmatrix} (xx) & (xx') & \cdots & (xx^{r-1}) \\ (x'x) & (x'x') & \cdots & (x'x^{r-1}) \\ \vdots & \vdots & & \vdots \\ (x^{r-1}x) & (x^{r-1}) & \cdots & (x^{r-1}x^{r-1}) \end{vmatrix} \begin{vmatrix} (xx) & (xx') & \cdots & (xx^r) \\ (x'x) & (x'x') & \cdots & (x'x^r) \\ \vdots & \vdots & & \vdots \\ (x^r x) & (x^r x') & \cdots & (x^r x^r) \end{vmatrix}}} \qquad (1) $$

$$ (i = 0,\ 1,\ 2,\ \ldots\ldots,\ n), $$

ici

$$ (x^i x^s) = x^i_0 x^s_0 + x^i_1 x^s_1 + \ldots\ldots + x^i_n x^s_n. $$

On voit donc facilement que

$$ ({}_ry\ {}_py) = 0, \quad (r \neq p) $$

$$ ({}_ry\ {}_py) = 1. \quad (r = p). $$

Par (1) on voit ainsi que y_i est une fonction de la variable t. Lorsque le point P décrit la courbe Γ, le point Q décrit en même temp la courbe ${}_r\mathfrak{S}$. Nous appellerons la courbe la $r^{ième}$ *courbe polaire absolue de* Γ. Soit Q' le point de ${}_r\mathfrak{S}$ qui correspond à l'autre point P' de Γ. La limite du rapport $\frac{arc\ QQ'}{arc\ PP'}$, quand P' tend vers P, s'appellera la $r^{ième}$ courbure de Γ au point P. Au lieu de la limite de $\frac{arc\ QQ'}{arc\ PP'}$ nous pouvons considérer évidemment la limite de

$$ \frac{sin\ \frac{\overline{QQ'}}{k}}{sin\ \frac{\overline{PP'}}{k}}. $$

Désignons cette limite par $\frac{1}{R_r}$ et en cherchons l'expression.

Or

$$ sin\frac{\overline{QQ'}}{k} = \sqrt{\frac{\begin{vmatrix} ({}_ry\,(t)\ {}_ry(t)) & (y_r(t)\ {}_ry(t+\triangle t)) \\ ({}_ry\,(t+\triangle t)\ {}_ry(t)) & ({}_ry(t+\triangle t)\ {}_ry(t+\triangle t)) \end{vmatrix}}{({}_ry(t)\ {}_ry(t))\ (y_r(t+\triangle t)\ {}_ry(t+\triangle t))}}, $$

$$ (r = 1,\ 2,\ \ldots\ldots,\ n-1). $$

De la formule (1) on tire

$$\sqrt{\frac{\begin{vmatrix} ({}_ry(t)\,{}_ry(t)) & ({}_ry(t)\,{}_ry(t+\triangle t)) \\ ({}_ry(t+\triangle t)\,{}_ry(t)) & ({}_ry(t+\triangle t)\,{}_ry(t+\triangle t)) \end{vmatrix}}{({}_ry(t)\,{}_ry(t))\ ({}_ry(t+\triangle t)\,{}_ry(t+\triangle t))}}$$

$$= \sqrt{\frac{\begin{vmatrix} (xx) & \dots (xx^{r-1}) & (xx^r) \\ \vdots & \vdots & \vdots \\ (x^{r-1}x) & \dots (x^{r-1}x^{r-1}) & (x^{r-1}x^r) \\ (x^rx) & \dots (x^rx^{r-1}) & (x^rx^r) \end{vmatrix} \begin{vmatrix} (xx) & \dots (xx^{r-1}) & (xx^{r+1}) \\ \vdots & \vdots & \vdots \\ (x^{r-1}x) & \dots (x^{r-1}x^{r-1}) & (x^{r-1}x^{r+1}) \\ (x^rx) & \dots (x^rx^{r-1}) & (x^rx^{r+1}) \end{vmatrix}}{\begin{vmatrix} (xx) & \dots (xx^{r-1}) & (xx^r) \\ \vdots & \vdots & \vdots \\ (x^{r-1}x) & \dots (x^{r-1}x^{r-1}) & (x^{r-1}x^r) \\ (x^{r+1}x) & \dots (x^{r+1}x^{r-1}) & (x^{r+1}x^r) \end{vmatrix} \begin{vmatrix} (xx) & \dots (xx^{r-1}) & (xx^{r+1}) \\ \vdots & \vdots & \vdots \\ (x^{r-1}x) & \dots (x^{r-1}x^{r-1}) & (x^{r-1}x^{r+1}) \\ (x^{r+1}x) & \dots (x^{r+1}x^{r-1}) & (x^{r+1}x^{r+1}) \end{vmatrix}}} \cdot \triangle t$$

$$= \sqrt{\frac{\begin{vmatrix} (xx) & \dots (xx^{r-1}) & (xx^r) \\ \vdots & \vdots & \vdots \\ (x^{r-1}x) & \dots (x^{r-1}x^{r-1}) & (x^{r-1}x^r) \\ (x^rx) & \dots (x^rx^{r-1}) & (x^rx^r) \end{vmatrix} \begin{vmatrix} (xx) & \dots (xx^{r-1}) & (xx^{r+1}) \\ \vdots & \vdots & \vdots \\ (x^{r-1}x) & \dots (x^{r-1}x^{r-1}) & (x^{r-1}x^{r+1}) \\ (x^rx) & \dots (x^rx^{r-1}) & (x^rx^{r+1}) \end{vmatrix}}{\begin{vmatrix} (xx) & \dots (xx^{r-1}) & (xx^r) \\ \vdots & \vdots & \vdots \\ (x^{r-1}x) & \dots (x^{r-1}x^{r-1}) & (x^{r-1}x^r) \\ (x^rx) & \dots (x^rx^{r-1}) & (x^rx^r) \end{vmatrix}}} \cdot \triangle t$$

$$+ \theta \triangle t,$$

ici $$\lim_{\triangle t \to 0} \theta = 0.$$

Par l'emploi du théorème de Sylvester, l'expression sous la radicale se déduit à

$$\frac{\triangle_{r-1}\ \triangle_{r+1}}{\triangle_r^2},$$

où

$$\triangle_i = \begin{vmatrix} (xx) & \dots & (xx^i) \\ \vdots & & \vdots \\ (x^ix) & \dots & (x^ix^i) \end{vmatrix} = \begin{Vmatrix} x_0\ x_1 & \dots & x_n \\ x_0'\ x_1' & \dots & x_n' \\ \dots & & \\ \dots & & \\ x_0^i\ x_1^i & \dots & x_n^i \end{Vmatrix}^2$$

D'autre part, nous avons

$$\sin\frac{\overline{PP'}}{k} = \sqrt{\frac{\begin{vmatrix} (xx) & (xx') \\ (x'x) & (x'x') \end{vmatrix}}{(xx)^2}} \cdot \triangle t + W\triangle t$$

$$= \frac{\sqrt{\triangle_1}}{k} \cdot \triangle t + W \triangle t ;$$

ici

$$\lim_{\triangle t \to 0} W = 0.$$

Par suite, la formule (1) qui donne la $r^{ième}$ courbure devient

$$\frac{1}{R_r^2} = k^2 \frac{\triangle_{r-1} \triangle_{r+1}}{\triangle_r^2 \triangle_1}.$$

En particulier, dans le cas euclidien, il faut considérer la limite de l'expression de la valeur de la courbure pour que $\frac{1}{k^2}$ tende vers zéro. Dans ce cas, en passant aux coordonnées cartésiennes $\mathfrak{x}_1 = \frac{x_1}{x_0}$, $\mathfrak{x}_2 = \frac{x_2}{x_0}$, ..., $\mathfrak{x}_n = \frac{x_n}{x_0}$, on aura

$$\frac{1}{R_r^2} = \frac{D_{r-1} D_{r+1}}{D_r^2 \, D_1},$$

où

$$D_i = \begin{vmatrix} (\mathfrak{x}'\mathfrak{x}') & \dots & (\mathfrak{x}'\mathfrak{x}^i) \\ \vdots & & \vdots \\ (\mathfrak{x}^i\mathfrak{x}') & \dots & (\mathfrak{x}^i\mathfrak{x}^i) \end{vmatrix} = \begin{Vmatrix} \mathfrak{x}_1' & \mathfrak{x}_2' & \dots & \mathfrak{x}_n' \\ \mathfrak{x}_1'' & \mathfrak{x}_2'' & \dots & \mathfrak{x}_n'' \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ \mathfrak{x}_1^i & \mathfrak{x}_2^i & \dots & \mathfrak{x}_n^i \end{Vmatrix}^2 .$$

La formule est déja obtenue par Brunel[1] et Landsberg.[2]

Maintenent, nous cherchons les formules dans l'espace qui doivent correspondre à celles de Frenet dans l'espace euclidien.

La différentiation de l'expression pour ${}_r y_i$ par rapport à t donnera

$$\frac{d_r y_i}{dt} = \frac{1}{\triangle_{r-1}^{\frac{3}{2}} \triangle_r^{\frac{3}{2}}} \left\{ \triangle_{r-1} \left(\begin{vmatrix} (xx) & \dots & (xx^r) \\ \vdots & & \vdots \\ (x^{r-1}x) & \dots & (x^{r-1}x) \end{vmatrix} \cdot \begin{vmatrix} (xx) & \dots & (xx^{r-1}) & x_i \\ \vdots & & \vdots & \vdots \\ (x^{r-1}x) & \dots & (x^{r-1}x^{r-1}) & x_i^{r-1} \\ (x^{r+1}x) & \dots & (x^{r+1}x^{r-1}) & x_i^{r+1} \end{vmatrix} \right. \right.$$

$$\left. \left. - \begin{vmatrix} (xx) & \dots & (xx^{r-1}) & x_i \\ \vdots & & \vdots & \vdots \\ (x^{r-1}x) & \dots & (x^{r-1}x^{r-1}) & x_i^{r-1} \\ (x^r x) & \dots & (x^r x^{r-1}) & x_i^r \end{vmatrix} \cdot \begin{vmatrix} (xx) & \dots & (xx^{r-1}) & (xx^{r+1}) \\ \vdots & & \vdots & \vdots \\ (x^{r-1}x) & \dots & (x^{r-1}x^{r-1}) & (x^{r-1}x^{r+1}) \\ (x^r x) & \dots & (x^r x^{r-1}) & (x^r x^{r+1}) \end{vmatrix} \right) \right\}$$

[1] Brunel, Math. Ann. 19.

[2] Landsberg, Crelle. 114.

$$-\triangle_r\left(\begin{vmatrix} (xx) & \dots & (xx^{r-1}) & x_i \\ \vdots & & \vdots & \vdots \\ (x^{r-1}x) & \dots & (x^{r-1}x^{r-1}) & x_i^{r-1} \\ (x^rx) & \dots & (x^rx) & x^r \end{vmatrix} \cdot \begin{vmatrix} (xx) & \dots & (xx^{r-2}) & (xx^r) \\ \vdots & & \vdots & \vdots \\ (x^{r-1}x) & \dots & (x^{r-2}x^{r-2}) & (x^{r-2}x^r) \\ (x^{r-1}x) & \dots & (x^{r-1}x^{r-2}) & (x^{r-1}x^r) \end{vmatrix}\right.$$

$$\left. -\begin{vmatrix} (xx) & \dots & (xx^{r-1}) \\ \vdots & & \vdots \\ (x^{r-2}x) & \dots & (x^{r-2}x^{r-1}) \\ (x^{r-1}x) & \dots & (x^{r-1}x^{r-1}) \end{vmatrix} \cdot \begin{vmatrix} (xx) & \dots & (xx^{r-2}) & (xx^r) & x_i \\ \vdots & & \vdots & \vdots & \vdots \\ (x^{r-1}x) & \dots & (x^{r-1}x^{r-2}) & (x^{r-1}x^r) & x_i^{r-1} \\ (x^rx) & \dots & (x^rx^{r-2}) & (x^rx^r) & x_i^r \end{vmatrix}\right)\Bigg\}.$$

Par l'emploi du théorème de Sylvester, on aura

$$\frac{d_r y_i}{dt} = \frac{1}{\triangle_{r-1}^{\frac{3}{2}}\triangle_r^{\frac{3}{2}}}\left\{\triangle_{r-1}^2 N_{r+1} - \triangle_r^2 N_{r-1}\right\};$$

ici

$$N_r = \begin{vmatrix} (xx) & \dots\dots & (xx^{r-1}) & x_i \\ (x'x) & \dots\dots & (x'x^{r-1}) & x_i' \\ \vdots & & \vdots & \vdots \\ (x^rx) & \dots\dots & (x^rx^{r-1}) & x_i^r \end{vmatrix}.$$

Par suite

$$\frac{d_r y_i}{ds} = \frac{{}_{r+1}y_i}{R_r} - \frac{{}_{r-1}y_i}{R_{r-1}}, \quad (r = 1, 2, \dots\dots, n-1) \qquad (2).$$

De même

$$\frac{d_0 y_i}{ds} = \frac{{}_1y_i}{k}, \quad \frac{d_n y_i}{ds} = -\frac{{}_{n-1}y_i}{R_{n-1}} \qquad (3).$$

Ce sont les formules cherchées. Dans le cas $n=3$, on aura les formules suivantes

$$\frac{d_0 y_i}{ds} = \frac{{}_1y_i}{R_0}, \quad \frac{d_1 y_i}{ds} = \frac{{}_2y_i}{R_1} - \frac{{}_0y_i}{R_0},$$

$$\frac{d_2 y_i}{ds} = \frac{{}_3y_i}{R_2} - \frac{{}_1y_i}{R_1}, \quad \frac{d_3 y_i}{ds} = -\frac{{}_2y_i}{R_2}.$$

Les formules sont déja obtenues par Bianchi.[1] En divisant les deux membres de l'équation (2) par k^2 et considérant les limites, il en suit les formules dans un espace euclidien

---

1 Voir Bianchi. Lezioni di Geometria Différenziale, p. 457. A. Razzaboni: Le formale del Frenet in geometria iperbolica e laro applicazioni. (Bologna, Gamberini 1897).

$$\frac{d\,{}_r a_i}{ds} = \frac{{}_{r-1}a_i}{R_r} - \frac{{}_{r-1}a_i}{R_{r-1}} \quad (i=0,\ 1,\ 2,\ \ldots,\ n) \qquad (4).$$

De même

$$\frac{d\,{}_1 a_i}{ds} = \frac{{}_2 a_i}{R_2}, \quad \frac{d\,{}_n a_i}{ds} = \frac{{}_{n-1}a_i}{R_{n-1}} \quad (i=0,\ 1,\ 2,\ \ldots.\ n) \qquad (5);$$

ici

$${}_r a_i = \frac{\begin{vmatrix} (x'x') & \ldots\ldots & (x'x^{r-1}) & x'_i \\ \vdots & & \vdots & \vdots \\ (x^r x') & \ldots\ldots & (x^r x^{r-1}) & x^r_i \end{vmatrix}}{\sqrt{\begin{vmatrix} (x'x') & \ldots\ldots & (x'x^{r-1}) \\ \vdots & & \vdots \\ (x^{r-1}x') & \ldots\ldots & (x^{r-1}x^{r-1}) \end{vmatrix} \cdot \begin{vmatrix} (x'x') & \ldots\ldots & (x'x^r) \\ \vdots & & \vdots \\ (x^r x') & \ldots\ldots & (x^r x^r) \end{vmatrix}}}.$$

$(i=\ 1,\ 2,\ \ldots\ldots\ n).$

On voit que

$$({}_r a\ {}_s a) = 0, \qquad (r \neq s);$$

$$({}_r a\ {}_s a) = 1, \qquad (r = s).$$

Les formules (4) et (5) ont été obtenues aussi par Brunel et Landsberg.

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